

## METHOD OF TRANSPORTING HEAVY CRUDE OILS IN DISPERSION FORM

### FIELD OF THE INVENTION

The present invention relates to the sphere of transportation of viscous effluents,  
5 notably crudes referred to as "heavy" crudes, for example because of their asphaltenes  
content.

### BACKGROUND OF THE INVENTION

There are known viscous crude transportation methods which consist in fluidizing  
the crude by heating, mixing with a fluidizing product, or treatment prior to  
10 transportation, for example bringing into an aqueous emulsion. However, these  
techniques are energy-consuming, or use complex processes that require large  
infrastructures which penalize the development of reservoirs.

In the present description, what is referred to as slurry is a suspension or a  
dispersion of solid particles in a liquid that can be circulated, notably by pumping. This  
15 slurry flow type is already commonly used during estuary or river dredging operations,  
and in the mining industry. What is most interesting is that it allows to transport a  
maximum amount of solid spoils with as little pumping energy as possible. Concerning  
the petroleum industry, slurry transportation is used to enrich fuels with coal particles  
and thus to increase their calorific value. The solid content can reach 60 % by mass  
20 while keeping acceptable flow properties.

## SUMMARY OF THE INVENTION

The present invention thus relates to a method of transporting a viscous petroleum effluent in pipes. According to the invention, the following stages are carried out :

- separating the effluent into at least a solid phase consisting of particles coming from  
5 the colloidal elements that act on the viscosity of said effluent and into a fluidized liquid phase,
- keeping an amount of particles dispersed in said fluidized liquid phase so as to obtain a suspension,
- circulating said suspension in the pipe.

10 The separation stage can be carried out by adding an amount of n-alkane such as butane, pentane, heptane.

The particles can be removed from the fluidized liquid phase.

The colloidal elements acting on the viscosity can be asphaltenes.

The particles can be dispersed through mechanical mixing.

15 The temperature of said circulating suspension can be controlled in order to slow down the dissolution of the particles in the effluent.

The temperature of the suspension can be kept below 40°C.

Said particles can be encapsulated after separation.

20 Said particles can be chemically modified prior to being dispersed in the fluidized effluent.

An additive can be added to disperse said particles.

A predetermined amount of a diluent for said liquid phase can be added.

A badly-solubilizing diluent can be selected for said particles.

The precipitated asphaltenes can be added in proportions ranging between 1 and

5 30 % by mass.

#### BRIEF DESCRIPTION OF THE FIGURES

Other features and advantages of the present invention will be clear from reading the description hereafter, given by way of non limitative examples, with reference to the accompanying figures wherein :

- 10 - Figure 1 compares colloidal and slurry solutions,  
- Figures 2 and 2a show the evolution of a slurry as a function of time,  
- Figures 3 and 4 show the influence of shear on a slurry,  
- Figures 5 and 5a show the influence of temperature on a slurry,  
- Figures 6a and 6b show the efficiency of the encapsulation of asphaltenes.

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#### DETAILED DESCRIPTION

The present invention preferably applies to heavy crudes. It thus consists in modifying the structural organization of the heavy crude which behaves like a viscous colloidal suspension, to obtain a suspension of non-colloidal particles of lower viscosity. The particles concerned by this change are, within the context of a preferred  
20 embodiment of the present invention, asphaltenes. Asphaltenes are molecules of higher

molecular weight contained in some crude oils. They are characterized by their high polarity and by the presence of polycondensed aromatic rings. The overlap of these particles spread out in the crude is greatly responsible for the high viscosity of the heavy crudes. This overlap can be eliminated by keeping the asphaltenes in form of solid particles precipitated in the crude. This configuration change can be obtained by deasphalting the crude, then by dispersing the precipitated asphaltenes in the base liquid, notably under strong mechanical stirring. A non limitative method of operation has been developed and it has been checked that the resulting morphology change of the crude in suspension form actually leads to a viscosity decrease. The protocol of the preferred embodiment first requires deasphalting the crude. Methods already exist to carry out this operation.

Advantageously, according to the invention, the asphaltene particles are transported in solid form in the crude base liquid in which these asphaltenes are dispersed so that the liquid obtained is more fluid than the original crude. Thus, transportation by pumping through the pipes is facilitated up to the refining plants. In these refining plants, the slurry is either fed as it is in these treating plants, or after a stage of separation of the suspended solid particles, the asphaltenes, which can simplify the downstream processes.

#### Example of a method of operation

The asphaltenes are precipitated by means of pentane according to the American standard ASTM 893-69. Once filtered (by means of sintered material of porosity 4) and dried (at 80°C for 2 hours), the particles are crushed (centrifugal ball crusher Retsch S 1000, 15 minutes at 350 rpm), then screened between 100 and 500 µm.

In order to obtain a slurry, or dispersion, the asphaltenes are dispersed in the deasphalted crude with a mechanical agitator RW20 IKA, at 1200 rpm for 20 minutes. The stirring paddle is selected for its high shearing power. It is a "bow tie" type serpentine paddle which allows excellent dispersion by means of the turbulence zone existing between its coils. The temperature of the sample is kept at 40°C. In each case described hereafter, 25 g product are prepared.

Test 1 : Comparison of two samples, one in colloidal suspension form and the other in slurry form

a) Two samples containing 10 % by mass of asphaltenes were prepared. The 10 asphaltenes are brought into the same deasphalted crude according to two different methods :

- one with the method of operation described above, which leads to a product in slurry form,
- the other by heating to 80°C for 1 hour, which leads to a product in colloidal solution 15 form. In this case, the viscosity is substantially that of a crude having 10 % asphaltenes.

The two samples are then observed under the same conditions with an optical microscope and their viscosity is measured by means of a rheometer (AR2000 type, of plane-plane geometry, with a 1-mm air gap). The results shown in Figure 1 (viscosity in Pa.s versus shear gradient G) confirm the morphology difference of the samples : no 20 particle is visible with the optical microscope for colloidal solution 1, whereas slurry 2 contains a large proportion thereof. The differences in viscosity V (Pa.s) of the samples (135 Pa.s for the colloidal solution and 40 Pa.s for the slurry) show the relevance of slurring the asphaltenes to decrease the viscosity of the heavy crudes.

b) A natural asphaltene-containing crude (with 17 % by mass of asphaltenes) is compared with a slurry obtained as above, but comprising 17 % by mass of asphaltenes. To be comparable, the two samples were heated to 40°C for 20 minutes. The colloidal crude has a viscosity of 345 Pa.s, whereas the slurry has a viscosity of 95 Pa.s. The efficiency of the method is clearly shown since the viscosity decrease is significant. It can be noted that the viscosity of the slurry in this case is relatively high for efficient transportation, a dilution would therefore be necessary.

Test 2 : Monitoring of the dissolution of the asphaltenes suspended in the slurry

In order to observe the behaviour with time of the morphology of a slurry, the rheologic and microscopic evolution of the sample containing 10 % asphaltenes in slurry is observed over a 146-day period. During this time, the sample is left to rest, at ambient temperature (20°C), and samples are regularly taken. Figure 2 shows the evolution of the viscosity of slurry 3 as a function of time. The various curves (3 to 8) show a progressive redissolution of the asphaltenes, which is translated into a viscosity rise up to the viscosity value of colloidal solution 9. Figure 2a gives the viscosity values as a function of time  $t$  in days, and the corresponding optical microscope photographs show the dissolution of the asphaltenes. However, this evolution at ambient temperature is slow, which allows to keep the benefits from the viscosity decrease for a flow in a pipeline during several hours.

20      Test 3 : Influence of shear on the dissolution of asphaltenes

The shear undergone by the slurry as it flows in a pipeline may disturb its morphology and annihilate too quickly the viscosity decrease generated. In order to evaluate the incidence of shear, various tests were carried out.

Two samples of a suspension in a slurry containing 10 % by mass of asphaltenes were prepared according to the protocol described above. One is left to rest, the other is stirred by means of a magnetic agitator and a bar magnet. The rheologic (viscosity in Pa.s) and morphologic evolution was followed in both cases. The results shown in 5 Figure 3 (viscosity as a function of t in days) by means of curve 10 which corresponds to a sample being stirred and curve 11 which corresponds to a sample at rest show no significant difference between the two samples.

Another test consisted in leaving a sample of a suspension in a slurry in the rheometer, under controlled shearing ( $50 \text{ s}^{-1}$ ), and in recording its viscosity throughout 10 the test, i.e. during approximately ten hours h. Figure 4 shows that, under such test conditions, no increase in viscosity V is observed during shearing for about 8 hours.

These two tests prove the absence of a strong influence of the flow on the change from a crude in slurry suspension to a colloidal suspension. It can also be noted that, if 15 the slurry configuration had been highly sensitive to shearing, it could not have been carried out because the sample preparation procedure requires very high shearing.

#### Test 4 : Influence of temperature on the dissolution of the asphaltenes

After showing that the crude slurry morphology is stable at ambient temperature ( $T=20^\circ\text{C}$ ), the influence of temperature is determined. In order to control its resistance to temperature, two samples containing 10 % asphaltenes were prepared according to 20 the procedure described and placed in a drying oven at  $40^\circ\text{C}$  and  $60^\circ\text{C}$ . Their rheologic and microscopic evolution is observed. The results of Figure 5 (ratio of the viscosity at time t to the viscosity at time 0:  $V_t/V_0$ , as a function of time h in hour) show that a temperature rise greatly favours the asphaltene dissolution kinetics, the kinetics being

shown by the slope of lines 12 (at 40°C) and 13 (at 60°C). Figure 5a shows the effect of temperature on a sample after 24 hours. Slurrying the heavy crude can require additional precautions or specific treatments to block or to slow down the dissolution of the asphaltenes in the crude if it has to be transported at a temperature above 40°C.

5        Test 5 : Preliminary encapsulation of the asphaltenes

In order to block dissolution of the asphaltenes to guarantee the stability of the slurry at the temperature and to be able thereafter to increase the amount of asphaltenes suspended, the asphaltenes can be advantageously encapsulated prior to being mixed with the crude. The complex coacervation method was used, described for example by  
10 J. Richard and J.-P. Benoît in "Microencapsulation" - Techniques de l'Ingénieur : Génie des Procédés; J 2 210, 1-20. The experimental protocol used is as follows : two 100-ml solutions, one containing 1 % gelatin, the other 1 % arabic gum, are prepared in milli-Q water and maintained at 40°C. The pH value of these two solutions is adjusted to 6.5. The asphaltenes are then dispersed in the gelatin solution using a Heidolph agitator for  
15 30 minutes, still at 40°C. A stirring rate of the order of 700 min<sup>-1</sup> is used. This is followed by a dropwise addition of the arabic gum solution (about 3 ml per minute). Then, the pH value of the mixture is adjusted to 4.5 by means of a 10 % acetic acid solution (predetermined volume). In order to allow the coacervate droplets to settle around the oil drops, stirring is maintained constant for one hour. Finally, the  
20 temperature of the system is lowered to 8 °C to allow the coacervate to gel. 2 ml glutaraldehyde is added and the pH value is finally adjusted to 9 by means of a 10 % sodium hydroxide solution (predetermined volume) and the whole system is left under stirring at 4500 rpm for 12 hours. The capsules obtained are then filtered, washed with water and toluene, and finally dried.

A slurry sample containing 10 % encapsulated asphaltenes was prepared and left in a drying oven at 40°C. Its resistance to temperature was checked by rheologic and microscopic monitoring. Figure 6a shows the structure of the encapsulated asphaltene suspension after 1 day and after 36 days. The results show that encapsulation has been  
5 efficient to block dissolution of the asphaltenes, the slurry configuration remaining intact after more than 30 days at a temperature of 40°C. A slight viscosity rise (from 50 Pa.s to 60 Pa.s) is observed. Figure 6b shows the structure of the non-encapsulated asphaltene suspension at the same times : the structure is no longer of the suspension type, and the viscosity becomes very high again.

10 Test 7 : Inerting the asphaltenes by surface polymerization

Still in order to block solvation of the asphaltenes when they are suspended, the precipitated asphaltenes are modified by acrylic acid. The acid adsorbed on the asphaltenes is then polymerized. 4 grams acrylic acid and 4 grams heptane are therefore added to 4 grams asphaltenes obtained by heptane precipitation and dried for two hours  
15 under vacuum. The suspension is stirred for two hours at ambient temperature in an inert atmosphere (argon). The excess acrylic acid is eliminated by filtration and the solid fraction is suspended again in 8 grams heptane. After addition of 0.04 g azo-bis-isobutyronitrile, the suspension is maintained for 4 hours at 60°C under stirring, still in an inert atmosphere. After filtration and washing with heptane, the modified asphaltenes  
20 are dried for 2 hours at 80°C. A slurry (sample No.1) consisting of 2 grams modified asphaltenes and 18 grams deasphalted crude is prepared according the procedure already described above. Another slurry (sample No.2) containing 2 grams non-modified asphaltenes and 18 grams deasphalted crude is prepared in parallel. These two

slurry samples are stored at 80°C and the evolution of their viscosity is monitored in the course of time.

- After a slight increase during the first storage hours of sample No.1, the viscosity stabilizes at a value that remains approximately three times lower than that of sample  
 5 No.2 after a week's storage at 80°C.

Sample	Storage time at 80°C (h)			
	0	2	5	170
Viscosity at 20°C (Pa.s)				
No.1	38	63	75	77
No.2	43	132	194	202

Modification of the asphaltenes allows to better control their capacity to be dissolved in the deasphalted crude.

#### Test 8 : Inerting the asphaltenes by surface change

- Changing the surface of the asphaltene particles by means of oleophobic  
 10 compounds allows to inhibit solvation of the asphaltenes. 4 grams of precipitated asphaltenes are added to 25 cm<sup>3</sup> perfluoroheptanoic acid. The suspension is stirred at ambient temperature for 2 hours. After filtration and washing with heptane, the asphaltenes are dried at 80°C for 2 hours.

- A slurry (sample No.3) consisting of 2 grams modified asphaltenes and 18 grams  
 15 deasphalted crude is prepared according to the procedure already described. A slurry (sample No.4) containing 2 grams non-modified asphaltenes and 18 grams deasphalted crude is prepared in parallel. These two samples are stored at 80°C and the evolution of their viscosity is monitored in the course of time.

The viscosity of sample No.3 remains approximately two times lower than that of sample No.4 after a week's storage at 80°C.

Sample	Storage time at 80°C (h)			
	0	2	5	170
Viscosity at 20°C (Pa.s)				
No.3	26	75	103	104
No.4	43	132	194	202

The method according to the invention can thus be clearly improved by treating the asphaltenes after their precipitation from the crudes.